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Silver Containing Sol-gel Coatings on Polyamide Fabrics as Antimicrobial Finish-Description of a Technical Application Process for Wash Permanent Antimicrobial Effect

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Abstract: This paper reports on an antimicrobial finishing for polyamide with high washfastness. As antimicrobial agent modified silica sols containing silver components are used as coating agent and are applied to the polyamide fabric by using a semi-industrial procedure. The antimicrobial properties of coated polyamide fabrics are determined against the bacteria *E. coli*. Significant antimicrobial effects are observed even after 40 washing cycles. The amount of silver on the polyamide fabrics was measured by using ICP-OES. Besides this, samples are investigated by means of UV/Vis-spectroscopy and scanning electron microscopy. Furthermore textile properties as, e.g., air permeability and mechanical properties were measured. Due to high antimicrobial effect and the strong washfastness of this finishing, this reported method could be of high interest for industrial production processes.

Keywords: Polyamide, Silver, Antimicrobial, Antibacterial, Biocides, Washfastness

Introduction

The treatment of textile materials with silver containing coatings is of high economic interest, especially because of possible applications in the medical sector leading to high prized products. Silver modified textiles are for example used in the treatment of atopic dermatitis [1] or are of interest as materials for antimicrobial wound bandages. Such wound bandages act as barrier against microbial attack and will promote the healing process this way [2,3]. Besides these antimicrobial applications a silver coating might yield conducting fibre surfaces which are of interest for protection against electromagnetic fields which are a serious risk for patients with pacemakers [4,5].

To apply antimicrobial properties onto fiber materials, applications of silver nanoparticles and colloidal silver are well known and the resulting antimicrobial properties have been reported several times [6-8]. Beside elementary silver particles, single Ag^+ ions can also be applied by complexation in cyclodextrin grafted onto cotton [9]. The deposition of silver nanoparticles can be enhanced by a corona-treatment of the fabrics or by layer-by-layer deposition [10,11].

A well known technique for textile modification is the sol-gel method [12,13], which allows the functionalization of textiles in a wide range of applications [14]. Based on the sol-gel approach also antimicrobial coatings for textile based on silver containing silica has been developed [15,16]. Starting from these first principal developments the now presented study will report on silver containing sol-gel coatings applied on polyamide fabrics as antimicrobial finish. The study will furthermore describe the technical application process for realization of a high washfastness of antimicrobial properties.

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Experimental

Sample Preparation

For application of sol-gel coatings onto polyamide fabrics three differently modified silica sols are used. All three silica sols are based on the same composition prepared by hydrolysis of tetraethoxysilane (TEOS) and 3-glycidyl-oxypropyltriethoxysilane (GLYEO) (both compounds are received from Wacker). For preparation of the silica sol, 10 m*l* of a mixture of TEOS and GLYEO (volume ratio of 7:3) are mixed with 60 m*l* of water and the mixture is stirred at room temperature. To the resulting turbid mixture 30 m*l* 0.01 molar HCl are added while stirring. Stirring is carried out until a clear solution is formed. After 24 h ageing at room temperature the resulting silica sol was employed for further modification to prepare antimicrobial properties. The specific modifications were carried out as follows:

Sol A: 100 m*l* silica sol were modified by adding 5.2 m*l* of an aqueous $AgNO_3$ solution (10 wt%) while stirring - the $AgNO_3$ is received from Carl Roth GmbH (purity ≥99 %)

Sol B: 100 m*l* silica sol were modified by dissolving 2 g of HTAT before 6.7 m*l* of water containing 1.7 g $AgNO_3$ are added while stirring - HTAT is hexadecyltrimethylammonium-p-toluenesulfonate $C_{26}H_{49}NO_3S$ and received from Merck (purity >99 %)

Table 1. Simplified description of the sols used for finishing as well as the curing temperatures

Name	Antimicrobial additive	Temperature for curing the applied coating
Sol A	$AgNO_3$	150 °C
Sol B	$AgNO_3$ and HTAT	140 °C
Sol C	Commercial colloidal silver and HTAT	130 °C

Sol C: 100 m*l* silica sol were modified by dissolving 2 g of HTAT, afterwards 50 m*l* of water containing 0.25 g colloidal silver are added while stirring - the colloidal silver is commercially available as powder (Fluka GmbH, No. 85131, EC No. 2311313) and exhibits a good dispersibility in water

The application of the three mentioned sols onto polyamide fabric is performed in a continuous pad-dry-cure process carried out with a coating device of ZeBes GmbH (Wolfen, Germany) commercially available. The curing is performed in a stream of hot air with temperatures set in the range of 130 °C up to 150 °C (see Table 1). The duration of curing is set to five minutes. The speed of coating process is set for all samples at 0.2 m/min. The polyamide fabric used is made from monofilament and exhibits a mass per unit area of 34.6 g/m^2.

Analytical Methods

Not only the untreated polyamide fabric was used as reference for following investigations but also a grey fabric that experienced a temperature treatment comparable to the finished samples (180 °C, 5 min). Stress-strain-behaviour of the fabrics was evaluated with a Zwick/Roell Zmart.Pro. The measurements were carried out according to DIN EN ISO 13934/1. Samples with a width of 50 mm were cut in grain of the fabric. The air-permeability was determined according to DIN53887 using a commercially available device (Company Frank). Before permeability measurements, the textile samples were climatised for at least 24 h. The size of textile samples is 20×20 cm and the volume of air passing through the textile was evaluated at a pressure of 2 mbar. The surface resistance of coated polyamide is determined according to DIN 54345 by using a commercially available Teraohmmeter Resitomat Type 2408 supplied by Burster. A detailed measurement set-up is depicted in following reference [14]. Before measurement the samples are climatized for at least 24 h (temperature of 20 °C and relative humidity of 65 %). The surface resistance is determined at eight different sample areas (front and back) and the average of these eight measurements is given. The optical properties of coated polyamide fabrics are investigated by UV/Vis-spectroscopy in arrangement of diffuse reflectance. A Varian Cary 5E UV-VIS-NIR Spectrophotometer equipped with an Ulbricht-Sphere was employed for the measurements. The investigations of the amounts of silver released from coated textile immersed in water were performed at 40 °C with a thermostatic dissolution tester (Pharma Test). Textile fabrics of the size 5×7.5 cm were stirred in 200 m*l* H_2O. As function of time samples were taken from the solution. The silver concentration of the solutions was determined with an ICP-OES spectrometer (Plasmaquant 110, Zeiss). To determine the total silver concentration on the coated fabrics, the fabrics are stirred into nitric acid for 12 h and afterwards the silver concentration in this solution is determined by ICP-OES. Scanning electron microscopy (SEM) was used to determine topographical details on the coated polyamide fabrics compared to the uncoated polyamide fabric. These SEM measurements are performed using a commercially available device (Hitachi S-3400N). The antibacterial activity of the coated polyamide fabrics is determined with *Escherichia coli* (gram-negative bacteria). For this purpose the fabrics are shaken with bacteria suspension and inoculated for 18 h at a temperature of 30 °C. Afterwards the fabrics are leached in phosphate buffer (pH=7) and the buffer is inoculated on agar plates. After two days the colony forming units are counted. The washfastness of the coated fabrics is tested with a commercial washing machine according to DIN EN ISO 6330 at 40 °C. For washing, an ECE washing powder (according to ISO 105-C08/C09, supplied by EMPA, Switzerland) is used. After this washing procedure, the textile fabrics are allowed to dry at room temperature.

Results and Discussion

General Changes of Textile Properties

It can be clearly observed that the appearances and properties of the polyamide fabrics are changed after the sol-gel application (Table 2 and Figure 1). The weight of textiles after coating increases slightly. This increase in weight is probably the result of applying small amounts of coating agent leading to thin coatings onto the fiber surfaces. The air permeability of the coated polyamide is decreased to a certain extent. However even if the polyamide fabric is only thermal treated without coating the air permeability decreased, this could be caused by a shrinking of fibres under the influence of heat. A coating applied - as carried out here - could enhance the decrease in air permeability by closing open spaces between the fibres. Compared to the values of the air permeability of the grey fabric this decrease is comparably low, only in the range of 20 % or less. This low decrease shows that no dramatic gluing of the open structure of the textiles has to be expected. This is also strengthened by the SEM micrographs shown in Figures 4-6. The pictures indicate coverage of the fibres but at least a slight gluing or bridging of adjacent fibres. The surface resistance of the polyamide fabric is significantly decreased by the applied silver containing coatings. This behaviour could be explained

Table 2. Textile properties of coated polyamide fabrics in comparison to the grey fabrics

Polyamide sample	Weight (g/m^2)	Air permeability (L/dm 1/min)	Surface resistance (Ohm)	Tensile strength (N)	Elongation at break (%)
PA with sol A	36.0	222 +/- 18	$6\ 10^{12}$	340 +/- 10	31 +/- 1
PA with sol B	36.0	188 +/- 6	$4\ 10^{10}$	250 +/- 40	36 +/- 7
PA with sol C	36.3	204 +/- 1	$4\ 10^{10}$	350 +/- 30	36 +/- 4
PA untreated reference	34.6	235 +/- 6	$8\ 10^{13}$	362 +/- 10	28 +/- 2
PA - 180 °C thermally treated reference	35.4	221 +/- 7	$6\ 10^{14}$	380 +/- 10	30 +/- 1

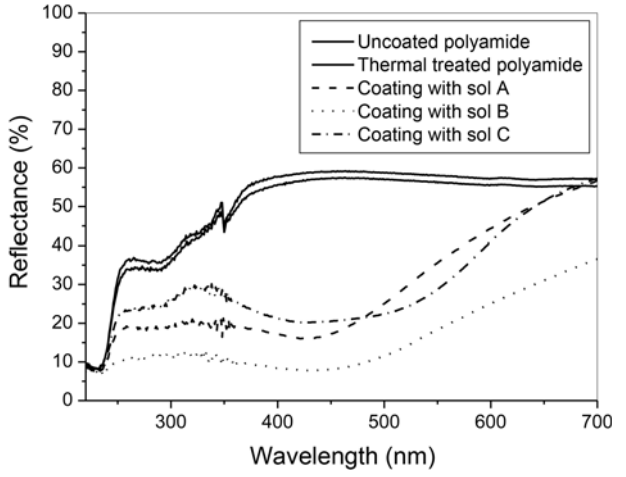

Figure 1. UV/Vis-spectra of coated and untreated polyamide fabrics.

by a higher moisture up-take from air by the modified silica coating [17] or by partly conductive properties as result of the applied silver particles, this would explain the lower surface resistance of $4{\cdot}10^{10}$ Ohm for coatings with sol B and sol C containing higher amounts of silver. However this decrease in surface resistance is not enough for applications as antistatic textiles or even as conductive textiles with purposes of electromagnetic shielding. Investigations of the stress-strain behaviour of the different fabrics were carried out to detect a possible weakening due to the treatment. The results show for samples A and C that there is at least a slight change in the tensile strength of the fabrics. While the untreated fabric exhibits a tensile strength of about 362 N, sample A has a tensile strength of 340, sample C of 350 N. The tensile strength of sample B decreases by about 29 % compared to the grey sample. A possible explanation might be that sol B is the one containing the highest amount of silver nitrate. Therefore a certain degradation of the polymer might occur due to the influence of aggressive species developing if the nitrate decomposes to nitrogenoxides. While the above mentioned changes in the properties would hardly influence the potential use of the coated textiles (at least for sol A and C), the appearance changed drastically after coating. This could limit the applications of the coated polyamide in everyday life for aesthetic reasons. However, e.g., for applications in the medical sector the colour is not limiting a possible use. The optical properties of the coated fabrics are mainly determined by the colour of the silver particles applied (see Figure 1). Nanoparticular silver causes a yellow coloration with an absorption maximum around 420 nm which is caused by the so-called plasmon resonance of elemental silver particles with sizes of few nanometers [18]. In case of sol A and sol B the silver particles result from a thermal reduction of $AgNO_3$ as reported earlier [15]. For both types of coating the minimum in the reflectance spectra (Figure 1) is at 428 nm which corresponds well to values reported for other silver nanoparticles. The reflectance minimum of sol B is stronger as expected, because the initial $AgNO_3$ concentration of this sol is higher than for sol A. In comparison coatings resulting from sol C contain a broader reflectance minimum, which can be easily explained because of the different silver source used.

Release of Silver and Antimicrobial Properties

For all coated polyamide fabrics the release of silver from the coatings is small. Even after 24 h stirring the amount of silver released is smaller than 9 wt% of the total silver that

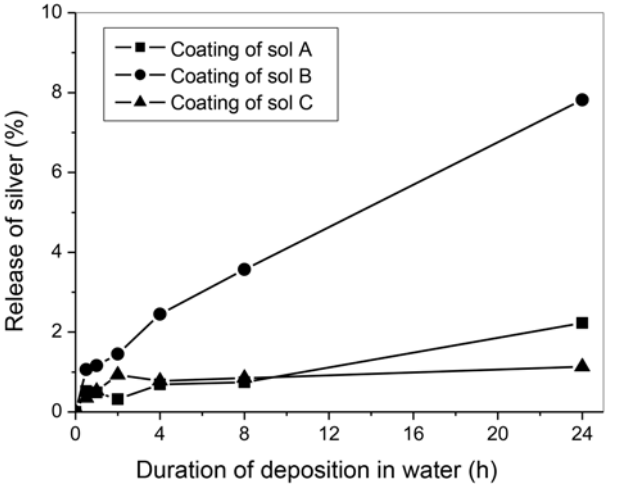

Figure 2. Time-depending release of silver from coated polyamide fabrics that were stirred in water. The release of silver is relative to the amount initially deposited.

Table 3. Summary of the antibacterial effect of sol-gel-coated polyamide fabrics against *Escherichia coli*. Results are shown for the samples as prepared and after up to 40 ECE washing cycles

Coating	Number of ECE washing cycles	Number of colony forming units, for different dilution of used bacteria suspension			
		10^5	10^4	10^3	10^2
Sol A	-	2	17	110	268
Sol A	5	0	0	0	0
Sol A	10	0	0	0	0
Sol A	40	2	7	54	>300
Sol B	-	0	0	8	41
Sol B	5	0	0	0	0
Sol B	10	0	0	0	0
Sol B	40	0	0	0	1
Sol C	-	0	0	0	0
Sol C	5	0	2	11	33
Sol C	10	2	25	140	>300
Sol C	40	12	141	>500	>500
Reference	-	23	139	>300	>500

has been deposited on the fabric (Figure 2). The low dissolution rate is a strong hint that the $AgNO_3$ used as silver source has been reduced to particles of elementary silver, as already indicated by the plasmon resonance described in the sub-chapter above. The small amount of silver released can also be taken as a hint that the silver particles - as well those probably formed in the sol as those formed after the application of the sol - are properly fixed on the textile by the silica coating. Obviously there is no removal of the coating material, neither silica nor silver, by mechanical impact due to the stirring of the textiles in water. The smallest release with only 1 wt% silver in 24 h stirring is reached with the sol C containing colloidal silver commercially available. In this case, silver particles are not developed during the process as for sol A and B, and therefore no residue of $AgNO_3$ can be expected (which would increase the amount of silver released due to the higher solubility of the salt). With sol B the highest silver release of about 8 wt% was observed, which could be explained by the highest amount of $AgNO_3$ used for preparation of this sol and the lower curing temperature compared to preparation with sol A.

The antimicrobial effect of the coated polyamide fabrics is reflected as decrease of colony forming units (Table 3). For all three samples the antimicrobial effect can be clearly determined, so it can be stated that even the lowest release of silver within this set of experiments is sufficient to achieve a good antimicrobial effect. It has to be remarked that after coating preparation the antimicrobial effect of sol A and sol B is lower compared to sol C. This difference could certainly be explained by the fact that the silver source is generally different compared to sol A and B, but it has to be kept in mind, that HTAT was used for dispersing/stabilizing the colloidal silver. Such quarternary ammonium compounds

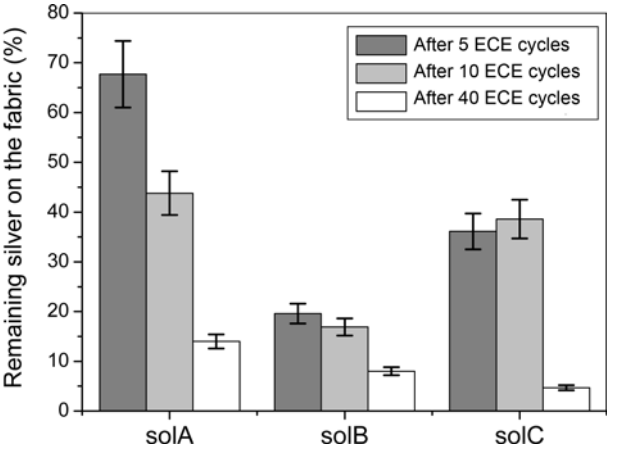

Figure 3. Amount of silver remaining on coated polyamide fabric after performing up to 40 ECE washing cycles. The amount of silver is relative to the amount initially deposited.

are well-known for a certain antimicrobial activity.

However after 5 ECE washing cycles the antimicrobial properties of coatings resulting from sol A increase, which might be explained by an activation of the surface of silver particles by the washing process. After 10 ECE washing cycles more than 50 % of silver have been removed from the polyamide during washing (Figure 3), however the antimicrobial effect of this coated textile is stronger compared to the freshly prepared sample. After 40 ECE washing cycles only 15 % of the silver deposited initially remain on the textile and the antimicrobial effect is significantly decreased but still present and detectable.

In comparison, polyamide fabrics treated with sol B exhibit a strong antimicrobial effect even after 40 ECE

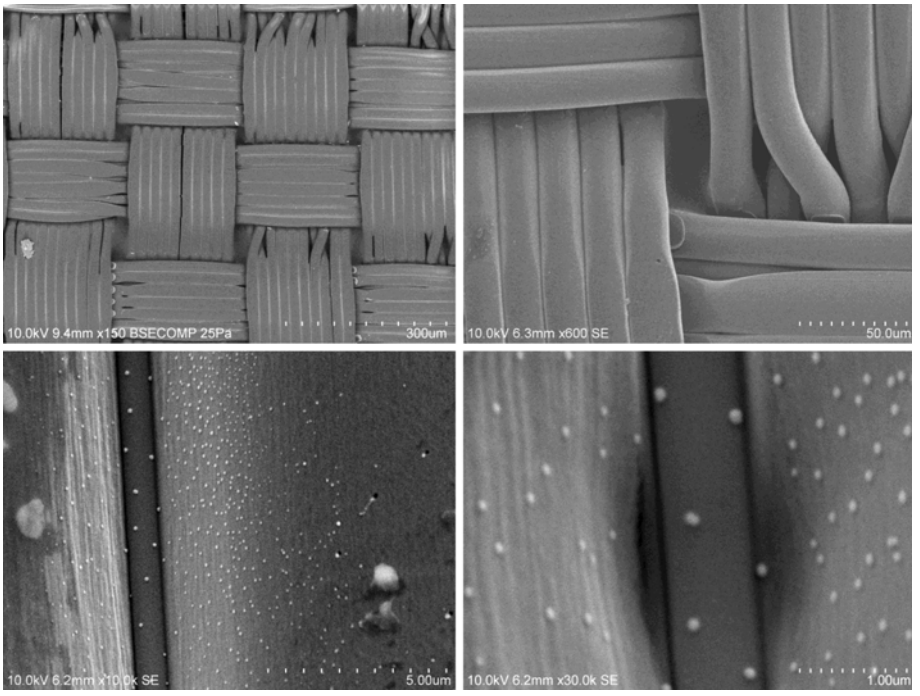

Figure 4. SEM images of polyamide fabric after treatment with sol A.

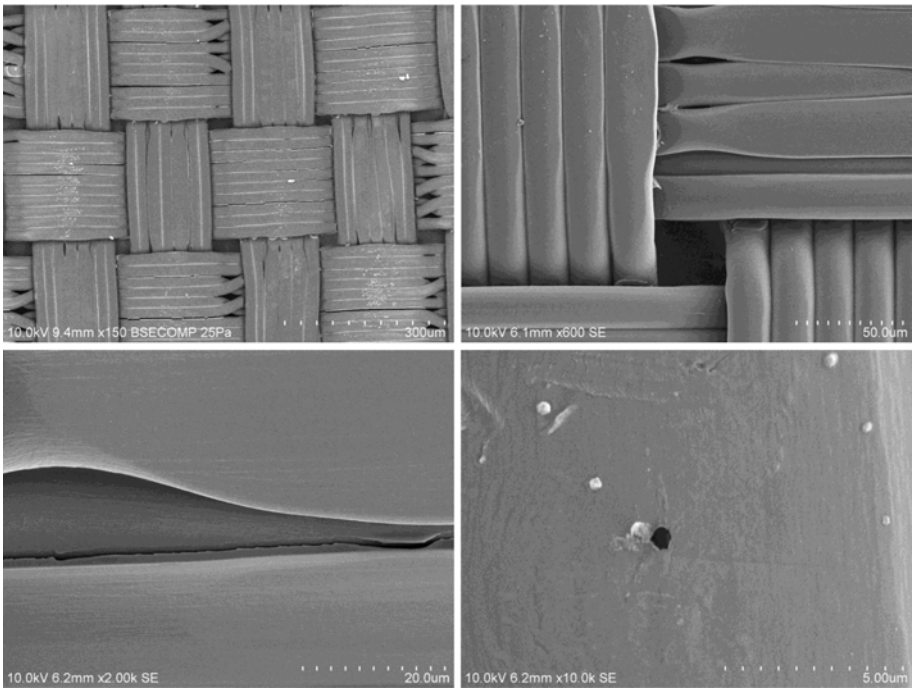

Figure 5. SEM images of polyamide fabric after treatment with sol B.

washing cycles, which could be explained by the higher concentration of $AgNO_3$ used for the coating preparation but also by addition of HTAT to this coating solution. HTAT as surfactant could lead to a more regular distribution of the coating and the silver particles on the fibers and could be by this responsible for a higher stability of the antimicrobial effect of these coatings. This suggestion is supported by comparison of SEM figures of textile coatings resulting from sol A and sol B (Figures 4 and 5). The application of sol A leads to a "dot-like" structure on the fiber surface, the

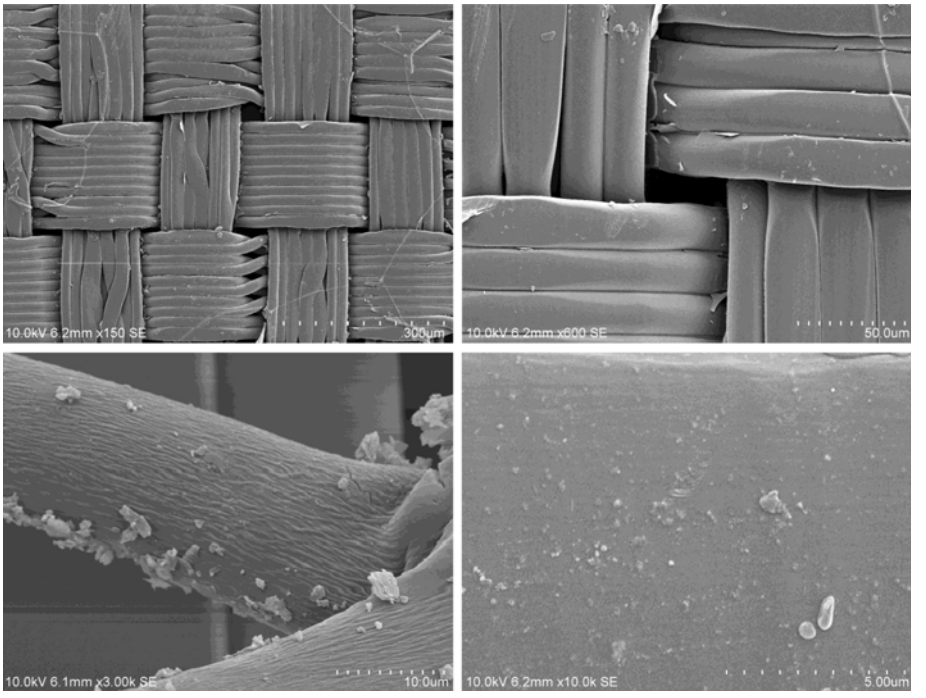

Figure 6. SEM images of polyamide fabric after treatment with sol C.

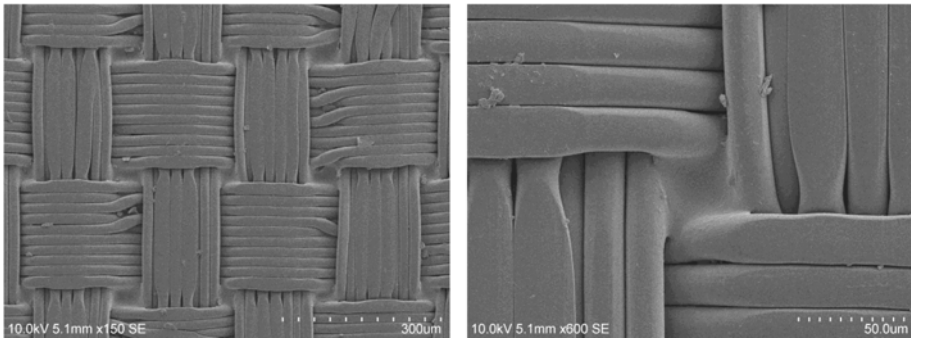

Figure 7. SEM images of the polyamide fabric without sol-gel treatment.

dots exhibit sizes below 100 nm (Figure 4). It can be estimated that these dots are silver particles, because pure silica sol coatings usually lead to smooth and not structured coatings on fibers. In comparison the SEM of coatings from sol B show only few silver dots (Figure 5), even though this sol contained an initially higher silver concentration. By this, it can be suggested that after application of sol B the applied silver is more regularly distributed onto the fiber surface and therefore the size of the silver particles formed is smaller. These smaller and more regular distributed particles seem to be fixed in a more stable way leading to a higher durability under the conditions of repeated ECE washing.

A totally different behaviour is shown by polyamide fabrics treated with sol C. These sample exhibit a good antimicrobial effect after preparation but achieve a smaller washfastness with a significant reduction in antimicrobial properties occurring after only five ECE washing cycles. This result corresponds to a strong reduction of the amount of the initially deposited silver to values of around 36 % after the first 5 ECE washing already. A small increase of silver as determined after 10 ECE washings to values of around 38 % is in the range of the estimated error bar. For this it can be stated, that after the first 10 ECE washings less than 40 % of silver is left. Further washing cycles up to 40 ECE cycles lead to a reduction of silver on the fabric to values smaller 5 %. By this it could be explained that after 40 ECE washing cycles, fabrics coated with sol C exhibit hardly no significant antimicrobial effect. This behaviour might be explained by using colloidal silver as silver source. This colloidal silver is probably not fixed that strong on the fabric as the in-situ prepared silver particles, which are resulting from the thermal reduction of $AgNO_3$. This statement

is supported by SEM investigations on these samples (Figure 6). By using sol C containing colloidal silver, the deposition of irregular particles of sizes up to micrometers can be observed. These big particles with a flake like structure might be easily abraded under conditions of repeated ECE washing cycles. For this, it could be stated, that the presented application of sol-gel coatings with in-situ formed silver particles could be a powerful mean to realize antimicrobial textiles with high wash fastness. General, it seems that the washfastness of antimicrobial effect increases by a decrease of size of applied silver particles, which will be investigated in further studies.

Conclusion

It was demonstrated that by a comparably simple technical application of silver containing silica sols for finishing polyamide textile, antimicrobial fabrics can be realized with strong antimicrobial effect and a high washfastness up to 40 washing cycles. The antimicrobial effect and the washfastness are significantly determined by the silver source used as additive to the silica sols. Due to the high washfastness this application method could be of interest for industrial application. Obviously, the washfastness decreases with increasing size of the silver particles deposited, probably due to a lower stability of these structures under the abrasive conditions of repeated ECE washing.

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